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Penning Ionization Electron Spectroscopy in Glow Discharge: a New Dimension for Gas Chromatography Detectors

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Admixtures to helium of 100 ppm and 5 ppm of nitrogen, and 100 ppm and 10 ppm of carbon monoxide were identified and measured in the helium discharge afterglow using an electrical probe placed into the plasma. For nitrogen and carbon monoxide gases, the measured electron energy spectra display distinct characteristic peaks (fingerprints). Location of the peaks on the energy scale is determined by the ionization energies of the analyte molecules. Nitrogen and carbon monoxide fingerprints were also observed in a binary mixture of these gases in helium, and the relative concentration analytes has been predicted. The technically simple and durable method is considered a good candidate for a number of analytical applications, and in particular, in GC and for analytical flight instrumentation.

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Introduction

Glow discharge (GD) plasma continues to attract increasing interest in analytical science and technology, mostly as a tool for atomization, excitation and ionization of the sample gas for subsequent analysis by means of a well-established technique such as atomic or mass spectroscopy. Indeed, the GD components – neutral and excited atoms and molecules, ions and electrons – bear various information about the nature of the gas transformed by the GD into the plasma. Some of this information can be extracted from GD without using an additional analytical technique, by measuring the discharge parameters. For example, the additive can be detected observing changes in the frequency of GD plasma oscillations.¹ Combining in a single GD cell tools for excitation and for analysis of the gas is advantageous for analytical applications where the apparatus size and weight considerations are crucial. Of the variety of such applications, analytical exobiology is a salient example.

Understanding the relationship between the chemical and physical evolution of the solar system and the appearance of life remains a principal goal of exobiology. For exobiology experiments onboard spacecraft or space probes, the detection and identification of a wide range of chemical species, over vast concentration ranges, is often a primary requirement. Miniaturization techniques or concepts are a top priority and provide one approach to addressing these issues. Advances in Gas Chromatography (GC) technology have produced very sensitive, tiny devices capable of detecting and identifying gases either in combination with GC or as a stand-alone instrument. For example, the Miniature Triaxial design Metastable Ionization Detector (mini-MID)² has an internal volume of 180 μL , sensitivity of 1 ppb and universal response. Additional advances to this Penning Ionization based detector have expanded its response range to over 10^6 and produced miniaturized microdetectors.

These detectors, although tiny, highly sensitive, with wide response range and universal response, do not provide any sample identification information other than the GC retention time. A GC detector providing sample identification independent of GC retention time identification

can reduce the number of columns required for a given analysis as well as increase the analytical capability of the instrument. Only a few analytical techniques, such as Mass Spectrometers (MS) and Ion Mobility Spectrometers (IMS)³, can provide sample identification independently from the GC retention time.

Here we present a method based on Penning Ionization Electron Spectroscopy (PIES) to provide a direct molecular identification of gas mixture components. In the described approach, the PIES electron energy spectrum is taken by means of a single electrode (probe) placed in the glow discharge plasma.

Background

Measurements of the kinetic energy of Penning electrons have been known since 1966⁴. This method is based on ionization of the target species by metastable helium atoms:



where He^* is a helium metastable atom, X denotes an atomic or molecular species, the analyte, and He and X^+ are the ground state helium atom and the molecular or atomic ion of the analyte species respectively. The reaction is energetically possible for all permanent gases except neon. For every molecule/atom, X, ionized by the helium metastables through reaction (1), an electron is produced, which we will refer to below as a PI electron, having a kinetic energy determined by:

$$\epsilon_x \approx E_m - E_x \quad (2)$$

Here E_m is the energy of the helium metastable atom ($E_m = 19.8$ eV for the 2^3S metastable state of helium) and E_x is the ionization energy for the species. Both E_m and E_x are atomic or molecular constants and therefore the PI electron energy, ϵ_x , is specific for each species and does not depend on the conditions of the experiment or on the presence of other species.

Considerable concentrations of metastable helium atoms, necessary for PI electron production, can be obtained using a gas discharge. A large fraction of the energy introduced into the helium gas by a discharge is deposited to metastable helium atoms and remains trapped there for a considerable period of time. Therefore, in the afterglow phase of the discharge, i.e. after the voltage initially applied to the discharge electrodes is terminated, a large number of helium metastable atoms continue to collide with analyte molecules and produce fast PI electrons according to reaction (1). These electrons may be collected by the probe - an additional electrode placed into the plasma. The energy of these PI electrons is measured by ramping a negative potential on the probe so that, at a particular time, only electrons having energies greater than the instantaneous potential of the probe contribute to the collector current. Electrons with lower energies are repelled away. The resulting current-voltage characteristic of the probe therefore bears information about the energy spectrum of electrons in plasma.

A comprehensive analysis for the Langmuir probe in plasma can be found in monograph.⁵ Experiments described below employ a cylindrical probe was placed at the axis of a cylindrical discharge tube (see Fig. 1). A detailed theoretical description for such cylindrically-symmetric geometry is presented in references^{6,7}. It is shown there that the area under a peak observed in the electron energy distribution function, i.e. the PI electron density near the probe, n_e , in certain conditions is proportional to the analyte concentration:

$$n_e = \int_{\epsilon_x} f(\epsilon) \frac{4\pi\sqrt{2\epsilon}}{m^{3/2}} d\epsilon \approx n_x \frac{k_x n_m b^2}{\mu_1^2 D(\epsilon_x)} \quad (3)$$

Here $f(\epsilon)$ is the electron energy distribution function (EEDF) on the tube axis, ϵ and m are the electron energy (in eV) and mass; n_x and n_m are the concentrations of the analyte and helium metastable atoms on the tube axis, respectively; k_x is the rate coefficient for reaction (1), b is the tube radius, $D(\epsilon)$ is the diffusion coefficient for electrons with energy ϵ , and μ_1 is the first root of Bessel function J_0 . In the derivation of equation (3), it was assumed that the electron energies

are much higher than the electron temperature of the bulk electrons in plasma ($\varepsilon_x \gg kT_e$). This condition is well satisfied in a discharge afterglow, i.e. a certain time after the voltage applied to GD is terminated. Another assumption used in the derivation of equation (3) is the requirement for chemi-ionization electrons to keep the same kinetic energy they were born with, when arriving to the probe. This assumption is valid when the time for electron diffusion across the tube, $b^2/\mu_i^2 D(\varepsilon)$, is much smaller than the energy relaxation time due to collisions with helium atoms, $1/(\delta v_a)$, i.e. when

$$b^2 \ll \frac{\mu_i^2 D(\varepsilon_x)}{v_a \delta} \quad (4)$$

Here v_a is the electron-atom collision frequency, and $\delta = 2m/M$ (M is the mass of helium atom).

Experimentally, the PI electron concentration, n_e , may be found by measuring the probe current. The second derivative of the probe current-voltage characteristic, $\frac{d^2 i_e}{du^2}$, is related to the electron energy distribution function through the Druyvesteyn relation^{5,6,7}:

$$f(\varepsilon) = \frac{m_e^2}{2\pi e^3 A} \frac{d^2 i_e}{du^2} \quad (5)$$

where e is the electron charge, A is the area of the probe, i_e is the PI electron current, and u is the probe voltage. Equations (3) and (5) link the analyte concentration, n_x , to the area under a peak observed in the dependence of second derivative of the current-voltage characteristic of the probe, $\frac{d^2 i_e}{du^2}$ vs. u . The analyte concentration is linearly dependent on the peak area (as given by equation 3), albeit the absolute value of the concentration can be calculated using equations (3) and (5), a prior knowledge about the PI rate coefficient, and the concentration of helium metastable atoms. The rate coefficient for reaction (1) is known for many species or can be measured by means of various techniques⁸ including the PIES method itself. The helium

metastable concentration can be obtained, as it will be shown below, from the same electron energy spectrum where peaks due to the analyte are observed, therefore the PIES spectra are self-sufficient for identification of the unknown admixture species and for the absolute measurement of its concentration.

The above analysis is developed for a specific case of the cylindrical Langmuir probe placed at the axis of the cylindrical discharge. The general conclusions, however, are valid for other probe/discharge geometries (such as a flat surface probe at the tube wall), which may have better sensitivity or resolution than the cylindrical probe and therefore could be preferable for specific analytical applications.

Limitations

Fundamentally, PI electron spectroscopy is based on identification of the electronic structure of molecules and belongs to the same class of analytical methods as, for example, Ultraviolet Photoionization Electron Spectroscopy (UPS)⁹. Although the basic concepts have been known since 1966 (as stated earlier), PIES is rarely used in modern analytical technology due to technical difficulties of the "classical" technique. A typical apparatus for direct observation of Penning Ionization spectra involves a high vacuum chamber with a beam of helium metastable atoms crossing a beam of analyte molecules. The method described in this paper effectively reduces this complex instrumentation to three small electrodes embedded into a GC capillary. Obviously, plasma is a more complex physical object than atomic and molecular beams, so a careful evaluation of the plasma parameters, potentially affecting sensitivity and resolution of the method, is required.

Spectrum broadening. Since the PI process occurs during a collision, with certain probabilities at certain distances between the collision partners, it leads to a distribution of electron energies that reflects the variation of the physical quantities during the collision. The act of ionization can be represented as a "vertical" transition from the initial potential term of the

quasi-molecule He^*X to the final potential term of the quasi-molecular ion HeX^+ . A transition leading to the ejection of a PI electron can occur at various internuclear distances, thus allowing for a certain spread of the PI electron energy around its asymptotic value, i.e. the ionization potential of the analyte molecule, E_x . The width of the PI electron energy distribution reflects the variation of the difference potential within the range of distances accessible in the collision. Depending on the relative positions of the initial and final collision terms and the probability of spontaneous ionization at a particular internuclear distance, the PI spectrum can be broadened and/or the maximum of the distribution shifted from their asymptotic value, E_x . The broadening is larger for a strong interaction between the metastable helium atom and the target particle, i.e. for a greater well depth of the interaction potential term⁴. Weak interactions lead to narrow distributions and small shifts from the asymptotic value. Penning ionization spectra for a number of molecular and atomic species were observed in molecular beam experiments^{9,10,11,12,13}. Most atoms, diatomic and simple molecules form weak interaction systems with He metastables and show PI spectra that are very similar to the photoionization spectra. The typical broadening in such cases do not exceed a few hundredths of an electron-volt⁹, however for complex polyatomic molecules, the spectra are often vibrationally unresolved and shifted. In summary, the analysis of experimental data on Penning ionization spectra shows that, in most cases of atoms and molecules comprising up to 20 atoms, these fundamental PI spectra are analogous to the photoionization spectra with peak widths of a 1-100 meV.

Sensitivity. An electrical discharge produces high concentrations of helium metastable atoms and the probability of Penning Ionization is significant, therefore the sensitivity of the method is potentially very high. Electric currents of 10^{-12} Amperes are measurable by standard electrometric techniques. Provided every PI electron from a volume of one cubic centimeter is collected by the probe, and there are no other electrons which contribute to this current, such a

current (10^{-12} A) corresponds to a rate of PI electron production, R_{min} , of 10^7 electrons per second. The upper sensitivity limit then may be estimated from:

$$\frac{n_x}{N} = \frac{R_{min}}{k_x n_m N} \quad (6)$$

where N is the concentration of the helium normal atoms. For a gas pressure of a few Torr ($N = 10^{17} \text{ cm}^{-3}$), the discharge produces approximately 10^{11} metastable helium atoms in the afterglow. For a typical value of k_x of $10^{-10} \text{ cm}^3 \text{ s}^{-1}$, one obtains a theoretical limit for the sensitivity to be one part per 10^{11} in a cubic centimeter of active volume. This very high sensitivity, however, should be understood as a baseline level for the approach. Sensitivities close to this value would be expected in ideal conditions such as in a crossed molecular beam experiment with single-electron-counting measurement technique.

Plasma factors. In plasma, broadening of the PI electron energy distribution occurs due to collisions with atoms of the buffer gas. Higher pressures provide increased density of the helium metastable atoms and the analyte molecules, which would lead to higher PI electron current to the probe, and therefore are desirable. However, for consistent identification of the analyte species, the electrons produced in the PI reaction should reach the collector having the same kinetic energy they were born with. This requirement imposes an upper limit on the total distance of travel for PI electrons, and thus on the radius of the discharge tube. The discharge tube radius should be smaller than the electron energy relaxation length, λ_e , given by the square

root of the RHS of equation (4) above: $\lambda_e = \sqrt{\frac{\mu_1^2 D(\epsilon_x)}{v_e + \delta v_a}} \approx \sqrt{\frac{\mu_1^2 D(\epsilon_x)}{\delta v_a}} = \lambda \delta^{-\frac{1}{2}}$. Note, that the

electron mean free path in a gas λ is much smaller than λ_e . Over the length of a mean free path an electron undertakes on average only one collision and loses only a small fraction $\delta < 10^{-4}$ of its energy. For helium, the energy relaxation range can be estimated as $\lambda_e = 10/p$ or $p\lambda_e = 10$, where p is the helium pressure in Torr and λ_e is in centimeters. To avoid energy relaxation of the

PI electrons and to obtain unbroadened peaks for each characteristic group of electrons in the energy spectrum, the electron path in the detector should be kept less than λ_e , which imposes the following restriction on the detector radius and helium pressure:

$$pb \ll 10 \text{ Torr}\cdot\text{cm} \quad (7)$$

So, for a tube diameter of ten millimeters, the helium pressure should be smaller than a few Torr. At a pressure of 100 Torr, the radius of the cell should not exceed 1 mm.

Other effects which can influence the PI electron energy spectrum measured by an electric probe in plasma include deviation of the electron velocity vector from the direction of the electric field near the probe surface, the current of Maxwellian bulk electrons, and the ion current. If an electron approaches the probe surface at a non-zero angle of incidence, then the retarding electric field would work against the normal component of the electron velocity only. Thus, if the normal component of its velocity is insufficient to overcome the barrier, the electron is repelled away from the probe, even though its total energy may be greater than the retarding potential of the probe. This factor leads to a loss in the number of PI electrons collected by the probe and affects sensitivity and, to some extent, resolution. The magnitude of this factor varies for different types of probes. In the experiments described below, this factor was found to be insignificant.

The electron energy distribution of the bulk electrons in an afterglow plasma is Maxwellian with a temperature close to that of the tube walls, i.e. $kT_e < 0.1 \text{ eV}$. The tail of this distribution may influence the PI electron energy spectrum at low electron energies but the contribution should not be important at $\epsilon > 1 \text{ eV}$. In addition to fast electrons, the probe at a retarding (for electrons) potential attracts positive ions (He^+). When saturated, the ion current is proportional to the probe potential, therefore, it does not contribute to the second derivative of the probe current. Only fluctuations of the ion current may be detected which are of the order of the average thermal energy of the ions. However, at low voltages, the ion current is not

saturated and varies exponentially with applied voltage (see Fig. 2). To obtain pure electron spectra, the ion contribution should be subtracted from the total signal. The ion component of the second derivative is modeled by

$$\frac{d^2 i_i}{du^2} = C_1 \exp\left(-\frac{C_2}{u}\right) + C_3, \quad (8)$$

and coefficients C_1 , C_2 and C_3 are determined by fitting the experimental data.

Broadening due to collisions with the buffer atoms and the current of positive ions are considered the most significant inherent plasma factors affecting sensitivity and resolution of the described analytical approach. It is estimated that the actual limit of sensitivity of the method is of the order of 1 ppb per cubic centimeter of the active volume. The typical value of spectral broadening is estimated at the level of 200 mV with a valley definition of 10%. Ionization energies range from 5 to 15 eV for most species corresponding to the range of PI electron energies of 10 eV. This yields a resolution of 50.

Experimental

To demonstrate this analytical technique, Penning Ionization Electron Spectra were measured in 99.9999% pure helium mixtures with 100 and 5 ppm of nitrogen and with 100 and 10 ppm of carbon monoxide.

A 20 cm long Pyrex glass tube of 18 mm internal diameter was used as a discharge cell (Fig. 1). It contained two cylindrical nickel discharge electrodes and a collector electrode-probe (a 10 mm long and 0.5 mm diameter nickel wire) placed approximately in the center of the tube. A glow discharge was formed in the cell by applying an electrical potential to the discharge electrodes. The current to the probe was measured in the afterglow, after the discharge voltage was set to zero. The high voltage power supply provided a DC voltage up to 3 KV at a current of up to 40 mA. The current-voltage characteristics of the probe were measured by an in-house designed electronic circuit, and the data was collected using a host computer. The circuit

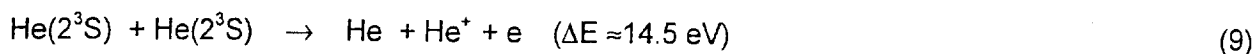
generated high voltage pulses to drive the discharge, ramped the probe potential and sampled the probe current in the discharge afterglow at chosen time instants. The electron energy spectra were measured electronically, using the traditional method of "second harmonic"⁶. In this method, a desired retarding potential is applied to the probe and mixed with a harmonically varying voltage of small amplitude, i.e. $V = V_0 + a \sin \nu t$. The amplitude of the AC component of the probe current measured at the double frequency, 2ν , is then directly proportional to the second derivative of the probe current (see ⁶ for details). Typical parameters of the circuit signals were: discharge driving voltage adjustable between 300 and 1500 volts; discharge pulse duration - from 10 to 100 microseconds; repetition rate - from 500 to 3000 Hz. The retarding potential, V_0 was adjustable between 1 and 20 Volts. The spectra were obtained by varying the retarding potential with increment of 0.1 Volt. The differentiating signal had an amplitude of $a = 1$ Volt and frequency $\nu = 1000 \text{ s}^{-1}$. The sensitivity and resolution of the spectra were determined by the parameters of the measurement circuit. The value of the differentiating signal amplitude, $a = 1$ Volt, determined the resolution for the measured spectra, as well as the sensitivity of the measurements, as shown in the Appendix. Resolution of one volt was sufficient to separate PIES spectra of nitrogen and carbon monoxide, providing good enough sensitivity to identify the analytes on the ppm level. Detection limits, spectral resolution and sensitivity of the method will be further defined and should improve with advanced developments of the detector.

Each point on the current-voltage characteristic is recorded over one discharge pulse. With discharge repetition frequency of 1 kHz and a retarding potential increment of 0.1 Volts, the single spectrum recording time was approximately 0.1 seconds. To improve signal-to-noise ratio, several scans may be required. Spectrum in Fig. 2 is an average over 10 scans.

PIES Spectra

In the first series of experiments, PIES spectra were observed in a mixture of 99.9999% pure helium and 104 ppm of nitrogen gas (Matheson Inc. certified). The absolute value of the second derivative of the probe current is presented in Fig. 2 by series #1. This is a combination of the fast electron current and the current of positive ions. Modeling the second derivative of the ion current with an exponent (equation 8, and series#2 in Fig. 2) and subtracting it from the measured dependence, a pure electron spectrum is obtained (series #3 in Fig. 2).

Figs. 3 and 4 show examples of electron spectra for nitrogen and carbon monoxide taken in an extended range for the probe potential, from 1 to 20 V. In all these spectra, there is a well-pronounced peak at 14.5 Volts. This peak is fundamental for the method - it is not related to analytes and is determined by the Penning-like ionization of two helium 2^3S metastable atoms in symmetric collisions:



Presence of this peak in PIES spectra provides an origin point for calibration of the electron energy scale (x-axis). The probe in plasma is at a certain non-zero potential, therefore there is a slight difference between the applied voltage and the energy of the electrons collected at this voltage. The plasma potential varies slightly with discharge current, gas pressure and the kind of analyte. In the experiments, the plasma potential was measured at zero applied voltage, and subtracted from all the applied voltages to give the "probe voltage" plotted in Fig. 2. Position of the helium peak at 14.4 V is in good agreement with a theoretical maximum¹⁰ of the PI electron energy distribution due to reaction (9).

In addition, the 14.4 V peak allows for calculation of the helium metastable concentration in the afterglow, N_m^0 , providing a basis for calculation of the analyte density through equations (3) and (5). The helium metastable atom density is a function of the discharge parameters, the

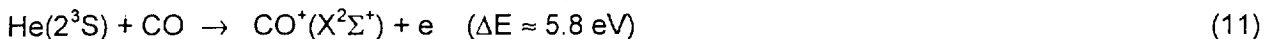
measurement delay time, and the concentration of the analyte. The peak at 14.4 V is proportional to the square of the helium metastable density concentration, thus by itself providing a sensitive response to the presence of additives in helium gas. Information provided by the 14.4 V peak to a certain extent is similar to that extracted from a MID detector.

Another common feature of the observed spectra is a steep rise at low (< 2 eV) electron energies. This is the tail of the Maxwellian distribution of the bulk plasma electrons. The fast electrons formed in binary collisions of helium metastable atoms and the slow Maxwellian electrons provide the upper (≈ 14 eV) and lower (≈ 2 eV) limits for the PI electron energies detectable in the described approach.

Besides the helium 14.4 V peak, the nitrogen (Fig. 3) and carbon monoxide (Fig. 4) spectra contain other peaks that are specific for the species. The main peak in the nitrogen spectra at 4.2 eV is due to reaction:



$\text{N}_2^+(\text{X}^2\Sigma)$ being the ground state of the nitrogen molecular ion. A similar reaction involving carbon monoxide creates electrons with energy of 5.8 eV:



A strong peak in the electron spectrum at this energy is observed in Fig. 4.

Fig. 5 displays a sample of PI electron spectra taken in a mixture of helium with 30 ppm of nitrogen and 70 ppm of carbon monoxide gases. Main peaks for nitrogen and carbon monoxide (at 4.2 and 5.8 eV, respectively) are well resolved and are present at the same positions as for the single mixtures.

Several secondary peaks may be observed in both nitrogen and carbon monoxide spectra, which are found to be either due to Penning ionization resulting in an electronically excited ion^{11,12,13}, or due to contaminants in the gas. For example a peak in the CO spectra at 3

volts (Figs. 4 and 5) is most probably due to ionization resulting in the 1π excited state of the molecular ion¹¹.

Quantitative

Provided the rate coefficients for the PI reactions are known, the absolute concentrations of the analytes can be extracted from the electron spectra applying the following scheme. First, for the peak at 14.4 eV, the density of the PI electrons near the surface of the probe, S_{He} , is calculated using the area under the peak and equation (5) and modified equation (3). This peak is due to the binary collisions of two metastable helium atoms given by reaction (9). For symmetric collisions, equation (3) should be modified to

$$n_{He} = k_{He} (N_m)^2 \frac{b^2}{\mu_1^2 D(14.4 \text{ eV})} \quad (12)$$

where k_{He} is the rate coefficient for reaction (9). It has been measured by several methods⁶. We used the originally reported¹⁴ $k_{He} \approx 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. Based on this value, and using an expression for the diffusion coefficient from monograph¹⁵, the concentration of $\text{He}(2^3\text{S})$, N_m , is calculated for each particular electron spectrum.

Secondly, the analyte concentration is found using equations (5) and (3). Obtaining concentrations of nitrogen from the data in Fig. 2 requires reliable knowledge about the rate coefficient of reaction (10). The authors are not aware of any measurements of this rate coefficient. Based on the data from our experiments and review [6], we accepted $k_{N_2} = 0.5 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Using this value, nitrogen concentrations of approximately 7 ppm for the 5 ppm mixture and approximately 300 ppm for the 100 ppm mixture were calculated. A rate coefficient for reaction (11) of $k_{CO} = 0.5 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ was reported in¹⁶. Using this value and the data from Fig. 3, we estimated concentration of carbon monoxide to be approximately 25 ppm and 180 ppm for the 10 ppm and 100 ppm mixtures, respectively.

The calculated values are systematically higher than the actual concentrations by a factor of two to three, which may be attributed to an uncertainty in the rate coefficients, and to certain deviations of the experimental apparatus from the requirements of the theory. Absolute concentrations of nitrogen and carbon monoxide were also calculated for the combined nitrogen and carbon monoxide spectrum (Fig. 5). To separate the CO and N₂ characteristic peaks, we described each peak with a model function:

$$\frac{d^2i}{du^2} = \left(\frac{d^2i}{du^2} \right)_{\max} \left(1 - \left(\frac{u - u_0}{\Delta u} \right)^2 \right)^{\frac{3}{2}} \quad (13)$$

which represents the instrument function for the experiments from reference ¹⁷, that are similar to ours. The peak height, $\left(\frac{d^2i}{du^2} \right)_{\max}$, its location, u_0 , are variable parameters and $\Delta u = a$. Fitting the experimental spectrum in Fig. 5 with two such functions, for the nitrogen and carbon monoxide characteristic peaks, gives estimates for the concentration of CO and N₂ in the mixture, separately. The calculated concentrations are 450 ppm of CO and 180 ppm of N₂. Although they are also significantly overestimated, the ratio of the concentrations is in a good agreement with the actual value.

In conclusion, a novel analytical method of Penning Ionization Electron Spectroscopy in plasma was demonstrated experimentally. Admixtures of nitrogen and carbon monoxide to helium were identified in single and binary mixtures at the 10 to 100 ppm level. The method is considered a promising candidate for development of a universal detector for gas chromatography. The technical simplicity, low size, weight and helium consumption of the instrument demonstrate the high potential of the PIES technique for a variety of analytical applications, and, in particular, for analytical space instrumentation. It should be pointed out, that PI electron spectra may be obtained in buffer gases other than helium. Other inert gases,

which form an excited or metastable state, such as argon or neon, could be prospective candidates for the method, or molecules with high enough ionization potential.

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Appendix.

Connection between the amplitude of the AC component of the probe current measured at the doubled frequency of the differentiating signal, $i_{2\omega}$, and the concentration of the analyte can be understood from the following considerations. As shown earlier^{6,17}, $i_{2\omega}$ is proportional to the second derivative of the probe current and the squared amplitude of the differentiating signal:

$$i_{2\omega}(\varepsilon) = \frac{a^2}{2} \frac{d^2 i_e}{du^2} \quad (\text{A.1})$$

Using Druyvesteyn relation (5), and the first part of equation (3), one obtains an expression for the PI electron concentration in terms of $i_{2\omega}$ and a :

$$n_e = \int_{\varepsilon_x} \frac{8\sqrt{2m} i_{2\omega} \sqrt{\varepsilon}}{e^3 A a^2} d\varepsilon = \int_{u_0-a}^{u_0+a} \frac{8\sqrt{2m} i_{2\omega} \sqrt{u}}{e^{3/2} A a^2} du \approx \frac{16\sqrt{2}}{3} \sqrt{\frac{m}{e^3}} \frac{\bar{i}_{2\omega}}{A a^2} \left((u_0 + a)^{3/2} - (u_0 - a)^{3/2} \right) \quad (\text{A.2})$$

The current amplitude $i_{2\omega}$ is assumed to be weakly dependent on the probe potential inside the range $[u_0-a, u_0+a]$. Using the second part of equation (3), the analyte concentration, n_x , could be expressed as:

$$n_x = \frac{16\sqrt{2}}{3} \sqrt{\frac{m}{e^3}} \frac{\mu_1 D(\varepsilon) \bar{i}_{2\omega}}{b^2 n_m k A a^2} \left((u_0 + a)^{3/2} - (u_0 - a)^{3/2} \right) \approx 19.5 \cdot 10^{12} \frac{D(\varepsilon) \bar{i}_{2\omega} \sqrt{u_0}}{b^2 A k n_m a} \quad (\text{A.3})$$

Equation A.1 demonstrates a typical relationship between the resolution and sensitivity: n_x is inversely proportional to the amplitude of the differentiating signal, a . Typical parameters in the described experiments were: $b=0.9$ cm; $D(\varepsilon) \approx 10^6 \text{ cm}^3 \text{ s}^{-1}$; $A = 0.16 \text{ cm}^2$; $a \approx 1$ V; $k \approx 10^{-10} \text{ cm}^3 \text{ s}^{-1}$; $n_m \approx 10^{12} \text{ cm}^{-3}$; $u_0 \approx 5$ V, which gives the following connection between the analyte concentration and the AC amplitude of the probe current:

$$n_x (\text{cm}^{-3}) \approx 3.4 \cdot 10^{18} i_{2\omega} (\text{A}) \quad (\text{A.4})$$

The noise level in the described experiments was of the order of 10^{-8} A which corresponds to a detection limit of $3.4 \cdot 10^{10} \text{ cm}^{-3}$, or 1 ppm at helium pressures of one Torr. This value is in a good

accord with a detection limit drawn from the spectra presented in figures 2-5. Further refinement of the measurement technique should lead to improved detection limit and/or spectral resolution of the method.

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Figures

Fig.1

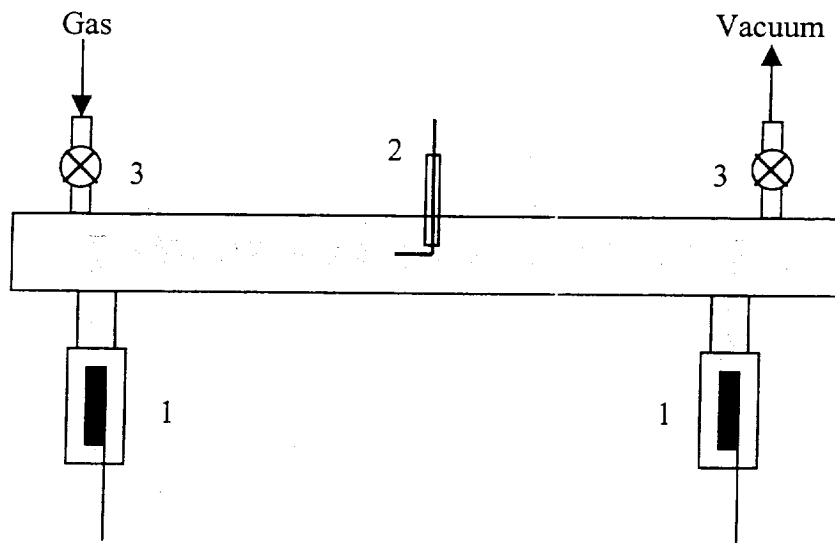


Fig. 2

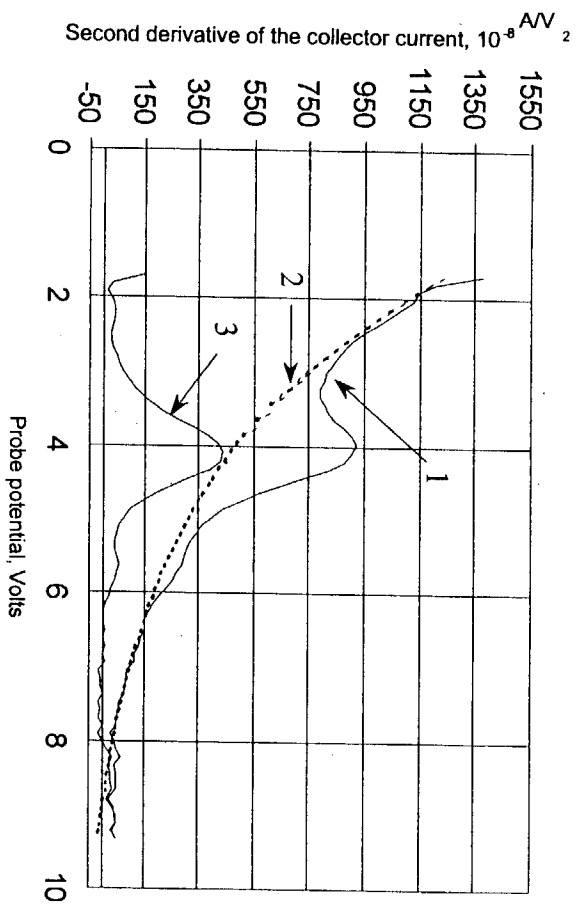
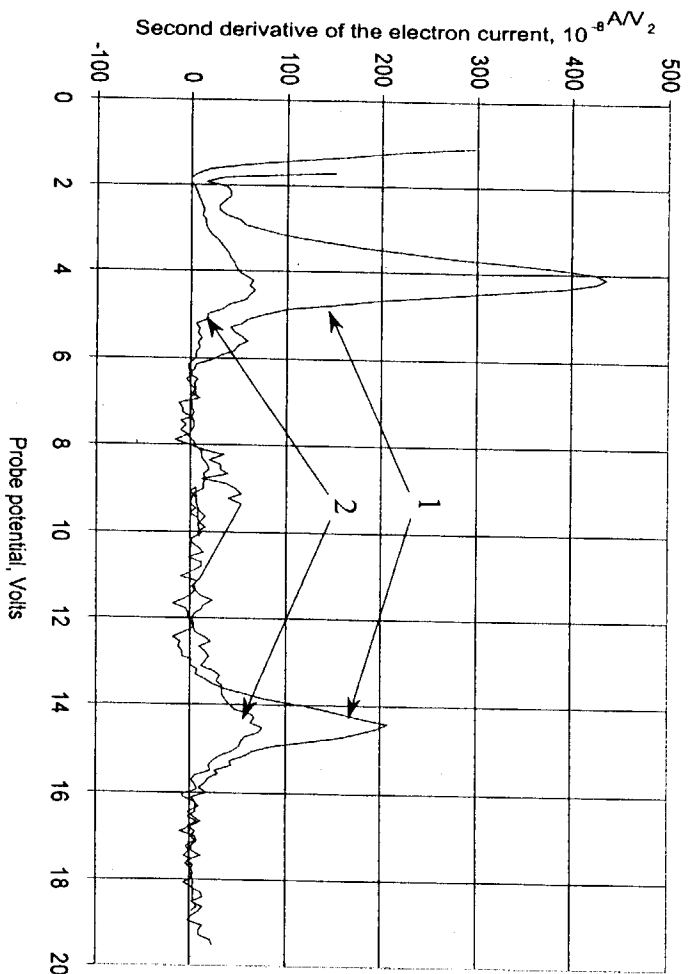


Fig. 3



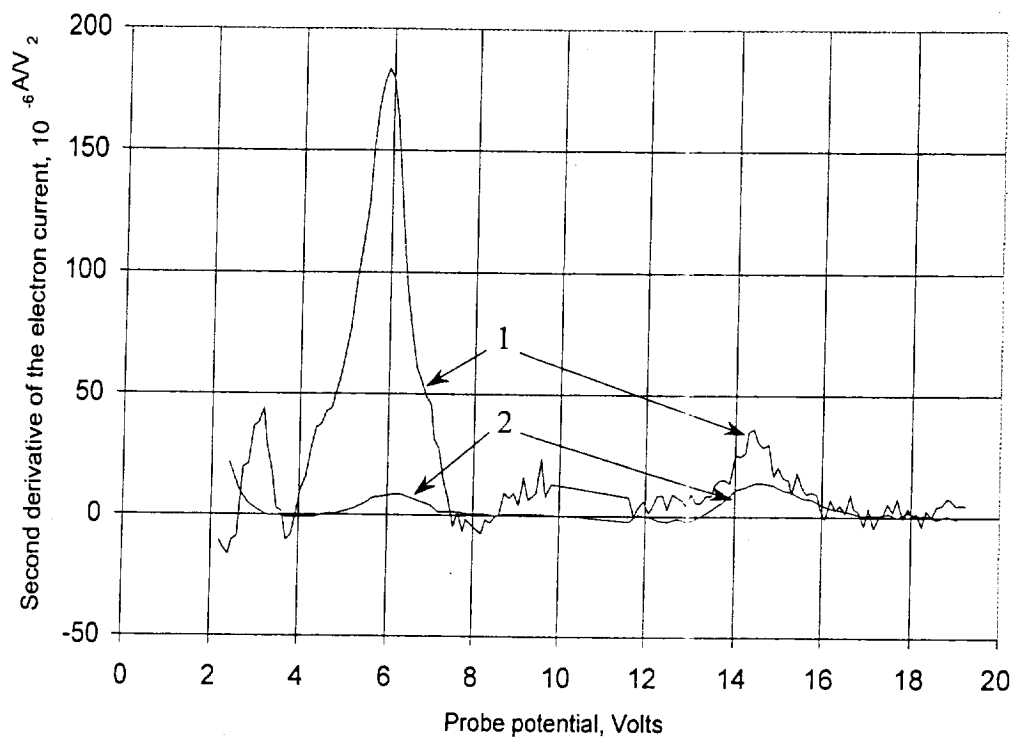


Fig. 5

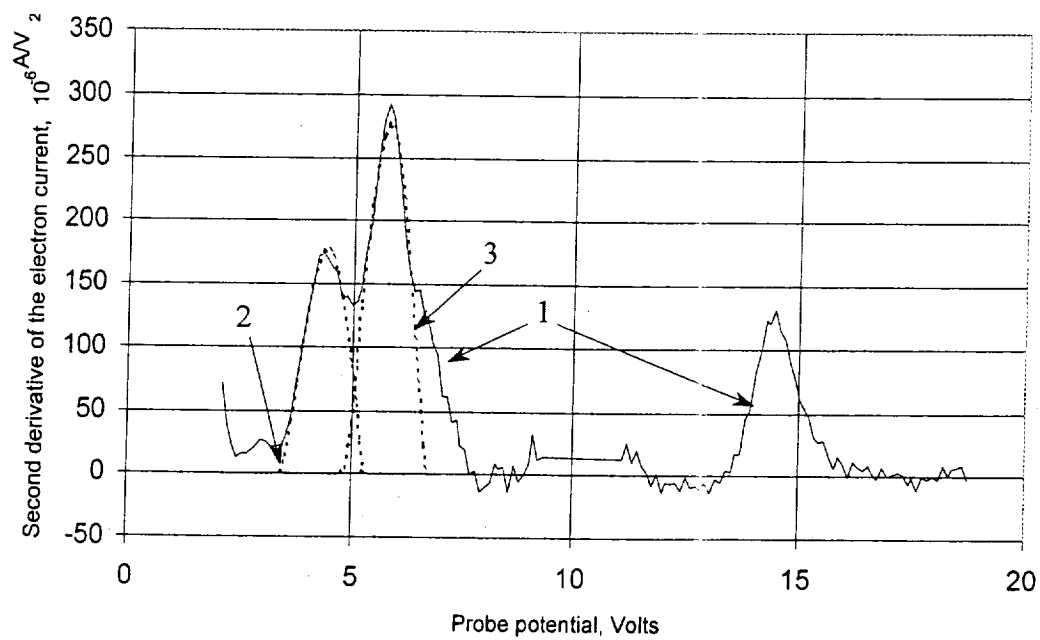


Figure captions

Fig. 1

Discharge cell. 1 – Discharge electrodes, 2 – Probe-collector, 3 – Vacuum valves.

Fig. 2

Spectra in 100 ppm of nitrogen. Series #1 - second derivative of the probe current; series #2 - ion current contribution (fitting using (10), where $C_1=2.42 \cdot 10^{-5} \text{ A/V}^2$, $C_2=2.86 \text{ V}$, $C_3=1.04 \cdot 10^{-6} \text{ A/V}^2$); series #3 - electron energy spectrum (series #1 minus series #2). Helium pressure: 0.5 Torr. Discharge current: 35 mA. Afterglow delay: 85 μs .

Fig. 3

Spectra of nitrogen. Series #1 – mixing ratio 100 ppm, helium pressure 0.5 Torr, discharge current 35 mA, afterglow delay 85 microseconds. Series #2 – mixing ratio 5 ppm, helium pressure 2.8 Torr, discharge current 18 mA, afterglow delay 175 μs .

Fig. 4

Spectra of carbon monoxide. Series #1 – mixing ratio 100 ppm, helium pressure 1.1 Torr, discharge current 8 mA, measurement delay 85 microseconds. Series #2 – mixing ratio 10 ppm, helium pressure 0.7 Torr, discharge current: 13 mA, afterglow delay 150 μs .

Fig. 5

Spectrum of 30 ppm N_2 + 70 ppm CO mixture (series #1). Helium pressure 0.5 Torr, discharge current: 20 mA, afterglow delay 85 μs . Fittings for nitrogen (series #2) and carbon monoxide (series #3) characteristic peaks are made using a model function given by (13).